Library

REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. X] *SECTION A* [NO. 2

AUGUST, 1939

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

A NOTE ON THE PREPARATION AND REACTIONS OF KARANJIN

By N. V. Subba Rao,
J. Veerabhadrarao and T. R. Seshadri
(*From the Department of Chemical Technology, Andhra University, Waltair*)

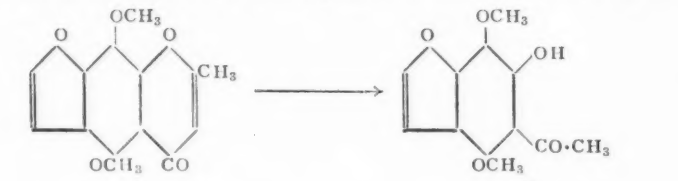
Received July 10, 1939

Karanjin, the bitter principle of the Pongamia oil, was first isolated by Limaye[1] by shaking the oil with alcohol. In our attempts to get large quantities of the substance for clinical use, we have examined different methods and found that extraction using industrial methylated spirits and the apparatus described in the experimental portion for continuous extraction is the most effective and economical. Karanjin was obtained in a yield of 0·9% ; but it should be pointed out that this good yield was obtained from the oil pressed from the seeds collected round about Waltair and that the yield varied with samples obtained from elsewhere. In one case there was very little Karanjin present. It has now been found that Karanjin is the active principle responsible for the curative action of the oil on leucoderma. When applied as a paste with any vegetable oil and rubbed, it stimulates pigmentation of the depigmented skin successfully. Karanjin does not taste bitter when the solid is placed straightaway on the tongue owing to the insolubility of the substance. But when a few drops of dilute alcoholic or aqueous alcoholic solution are employed, the taste is bitter and is associated with a peculiar tingling effect. The bitterness is quite mild as compared with the taste of Psoralen, Isopsoralen and Naringin.

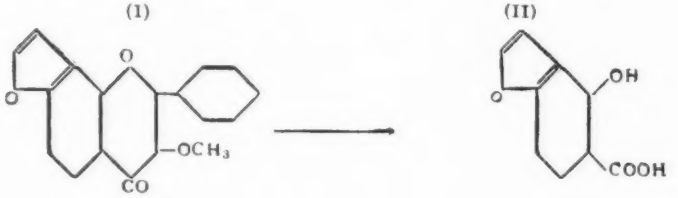
The alkaline hydrolysis of Karanjin has been shown by Limaye[2] to give rise to four fission products : (1) Benzoic acid, (2) Karanjic acid (4-hydroxy-coumarone-5-carboxylic acid), (3) C-acetyl karanjol (4-hydroxy-5-acetyl-coumarone) and (4) Karanjol (4-hydroxy-coumarone). But the experimental details regarding the hydrolysis have not been published by him. We had occasion to examine the different methods of hydrolysis but meanwhile Manjunath *et al.*[3] reported that by using alcoholic potash a mixture of (2) and (3) are obtained, C-acetyl karanjol being the main product, whereas, Karanjic acid was obtained in very poor yields. Our results agree with this observation. Further, we noticed that fusion with potash produced considerable destruction of the substance and only benzoic acid could be detected amongst the products. By employing boiling aqueous alkali for

the hydrolysis, Karanjic acid was easily obtained as the only product along with benzoic acid. But the action of dilute aqueous alkali was very slow and a large portion of Karanjin remained unaffected even after boiling for several hours. The reaction was considerably expedited by adding some alcohol in order to increase the dissolving power.

Working with Kellins, a chromono-furan having the constitution (I) Späth and Gruber[4] found that one per cent. aqueous potash reacts smoothly in the course of half an hour to give rise to a good yield of kellinone, the corresponding ketone (II). The same effect was observed by Fantl and Salem[5] when they used aqueous barium hydroxide for the hydrolysis of kellins. Adopting exactly the same procedure and excluding air as much as possible, we found that Karanjin (III) undergoes decomposition in a different way and produces only Karanjic acid (IV) in addition to benzoic acid and the ketonic product is not produced in any appreciable amounts.



(I) (II)



(III) (IV)

Desai, Sudborough and Watson[6] obtained a deep yellow precipitate possessing the properties of proteins when Pongamia oil was treated with 2% of a mixture of 2 parts of sulphuric acid and one of water. It was reported to have turned white on washing with water and to have been incapable of being crystallised. On repeating the experiment, it was noticed by us that no amorphous substance could be obtained and that a crystalline precipitate of potassium sulphate was formed instead. That potassium was present in some form in the oil was confirmed by slowly ashing the oil and detecting potassium in the ash. The metal was further proved to be present in the ash of the seed kernel.

Karanjin undergoes mercuration with mercuric acetate in methyl alcoholic solution to form a sparingly soluble product. It is noticed that

two acetoxy-mercury groups have entered into combination but their position in the Karanjin molecule has not yet been ascertained.

Experimental

The seed of *Pongamia glabra*, as it is obtained fresh, consists of an external woody shell within which is lodged the kernel. After drying, the outer shell could be easily removed by gentle hitting with a hammer. The following are the results of proximate analysis of air-dried kernels. The methods employed are those adopted by the Association of the Official Agricultural Chemists.

		%
Moisture	..	19
Oil	..	27·5
Starch	..	6·6
Crude fibre	..	7·3
Proteins	..	17·4
Ash	..	2·4

Potassium sulphate from the oil.—

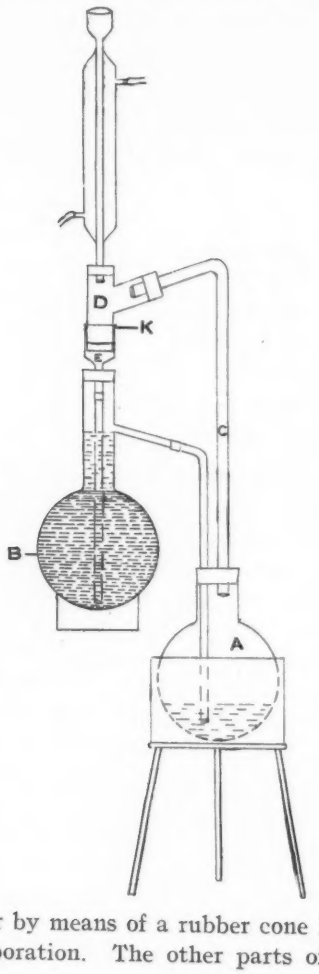
50 g. of the oil were shaken well with 4 c.c. of a mixture of 2 parts of concentrated sulphuric acid and one of water. The oil assumed a bright orange colour and a solid was observed to deposit slowly. The mixture was set aside for 24 hours to ensure complete precipitation of the solid. It was filtered and the residue on the filter washed with petroleum ether and then with benzene. The solid was then recrystallised from water when rhombic crystals of potassium sulphate were obtained. It gave a lilac violet colouration when introduced into the flame on the platinum wire, a precipitate with perchloric acid, and with sodium cobaltinitrite. No protein, as reported by Desai, Sudborough and Watson, could be isolated.

With a view to confirm the presence of potassium in the oil, the ash of the oil was prepared. It formed 0·25% on the weight of the oil and contained potassium and iron.

Isolation of Karanjin.—

Pongamia oil obtained by pressing the kernels in a country-press was filtered to remove suspended impurities and used for the isolation of Karanjin with the apparatus given in the accompanying diagram. It is a modification of the apparatus found in Gattermann's *Laboratory Methods of Organic Chemistry* and it makes the extraction less tedious and more efficient. The chief feature to be noticed is that the tube C conveying the vapours of the solvent (alcohol) from flask A is made as short as possible by connecting it

to the bottom of the reflux condenser instead of to the top and consequently the solvent in a rather warm condition extracts the oil kept in the flask B. D and E are glass three-way tube and adapter respectively which are



connected to each other by means of a rubber cone K. This prevents loss of the solvent by evaporation. The other parts of the arrangement are easily understood.

Using a litre distilling flask as a container for the oil (900 g.), extraction was carried on for 30 hours, when a good yield of Karanjin was obtained. The alcoholic extract was coloured brown and a small quantity of the oil was also carried over along with Karanjin into the flask A. At the end of

the experiment, a crystalline solid settled down when the alcoholic extract was allowed to cool. However, the solution was concentrated by distilling away most of the solvent and then set aside for crystallisation. The crystalline solid was filtered, washed with a little petroleum ether and finally recrystallised from alcohol. Karanjin was thereby obtained as colourless rectangular plates melting at 158–9° C. The yield was 8·0 g. (about 0·9%). (Found : C, 73·5 ; H, 4·2%, $C_9H_6O_2$ requires C, 74·0 ; H, 4·1%.) The molecular weight of the substance was determined by Rast's method using camphor and the value obtained was 283 (compare Manjunath *et al.*, 285). This value therefore agrees with the molecular formula $C_{18}H_{12}O_4$, the required figure being 292.

Karanjin is easily soluble in ethyl and methyl alcohols, benzene and petroleum ether. Concentrated sulphuric acid dissolved it forming a yellow solution which turned red and finally green when heated to 100° C. On dilution with water, Karanjin was produced unaltered.

The oil left after treatment with alcohol as described above became quite transparent. It was noticed that this contained very little of unsaponifiable matter obviously due to their removal by alcohol.

Hydrolysis of Karanjin.—

Preparation of Karanjic acid.—Karanjin (2 g.) was treated with 3% aqueous alcoholic potash (alcohol 100 c.c., water 150 c.c., potash 7·5 g.) in a litre flask and after displacing all the air with nitrogen boiled under reflux, whereby a reddish yellow solution was produced. All the Karanjin went into solution within the first half hour. At the end of 3 hours, as much alcohol as possible was distilled off and the aqueous solution acidified with dilute sulphuric acid (200 c.c. of 4% acid). The colourless precipitate that was obtained was filtered and dried in air (yield 0·9 g.). It crystallised from 50% alcohol as rectangular rods and melted at 216–18° C. with decomposition. (Found : C, 60·9 ; H, 3·2%. $C_9H_6O_4$ requires C, 60·7 ; H, 3·4%.) The substance gave a blue colouration with ferric chloride and dissolved in both sodium carbonate and bicarbonate solutions. It agreed with the description of karanjic acid given by Manjunath *et al.*

The aqueous filtrate left after the removal of crude Karanjic acid was repeatedly extracted with ether and the ether extract evaporated to dryness. The residue was dissolved in aqueous sodium carbonate and by extracting this with a little ether, a very small quantity of a brown oily liquid was obtained. It was, however, in too small a quantity to be identified. The sodium carbonate solution was then strongly acidified with

hydrochloric acid, when a grey solid melting at 115° C. was obtained. When this was boiled with water a small quantity was left undissolved. This melted at 210° C. with decomposition and was obviously karanjic acid. By ether exctracting the aqueous solution and removing the ether from the extract, a colourless crystalline solid melting at 120° C. was obtained and this was identified as benzoic acid.

Trials using 1% aqueous potash and otherwise observing the above conditions gave karanjic acid in a yield of 0·4 g. about half the quantity of Karanjin being left unaffected. Employing 2% and 3% alkali solutions the hydrolysis was better but still 30% and 20% respectively of the original Karanjin was left unaffected.

Mercuration of Karanjin.—

Karanjin (0·5 g.) was dissolved in anhydrous methyl alcohol (50 c.c.) and added to a solution of mercuric acetate (7·5 g.) in anhydrous methyl alcohol (120 c.c.) and boiled under reflux for 20 hours. The contents of the flask were filtered to separate the yellow mercurated product which was washed repeatedly with methyl alcohol. It was then dried and analysed. The yield was 0·4 g. (Found : Hg, 50·1%. $C_{18}H_{10}O_4$ ($Hg.O\cdot CO\cdot CH_3$). or $C_{22}H_{16}O_8\ Hg_2$ requires Hg, 49·6%.) The product obtained was therefore diacetoxy-mercuri-karanjin.

Summary

A method of extracting Karanjin in good yield from Pongamia oil is described. Karanjin is only faintly bitter and is found to be useful for the treatment of leucoderma. A method of hydrolysis of Karanjin giving rise to a good yield of Karanjic acid has been found. It has been shown that Pongamia oil contains potassium in some form of chemical combination. By the action of mercuric acetate, Karanjin yields a di-acetoxy-mercuri compound.

REFERENCES

1. Limaye .. *Abst. Proc. Ind. Sci. Congress*, 1925, 118.
2. ——— .. *Ibid.*, 1926, 151.
Rasayanam, 1936, 1–14 and 1937, 119.
3. Manjunath, Seetharamiah & Siddappa — *Ber.*, 1939, **72**, 93.
4. Späth and Gruber .. *Ibid.*, 1938, **71**, 106.
5. Fantl and Salem .. *Biochem. Zeit.*, 1930, **226**, 166.
6. Desai, Sudborough and Watson — *Jour. Ind. Inst. Sci.*, 1923, **6**, Part V, 93–110.

RAMAN SPECTRA OF FUSED NITRATES

By P. A. Moses

(From the Department of Physics, Andhra University, Waltair)

Received July 21, 1939

(Communicated by Prof. S. Bhagavantam)

1. Introduction

Several authors have studied the Raman spectra of inorganic nitrates in the crystalline state. Sodium nitrate crystals in particular have formed the subject of intensive investigation by a number of workers.[1–10] Of these authors, only Schæffer, Mattossi and Aderhold, Nisi, Cabannes and Canals, Pattabhiramayya and Nedungadi worked with single crystals. All the others used powdered crystals. Considerable amount of work has also been done in aqueous solutions of nitrates by some of the above-mentioned authors and certain others.[11–16]

Although the nitrates in the solid and dissolved states have been studied in such an extensive manner, comparatively less attention appears to have been given to the nitrates in the fused state. Thatte and Ganesan[17] and Rao studied the Raman spectra of some fused nitrates. The results obtained by these investigators are incomplete and they have not published any pictures of the Raman spectra obtained in the fused state. It is presumed that the abundance of the continuous spectrum in the scattered light has prevented these authors from pursuing such studies in greater detail. It is only recently, that Nedungadi has published a picture of the Raman spectrum of sodium nitrate in the fused state, in which, some of the prominent features characteristic of the liquid state are present. He has not however made any quantitative study of either the polarisation characters of the Raman lines or the intensity distribution in the wings accompanying the Rayleigh lines.

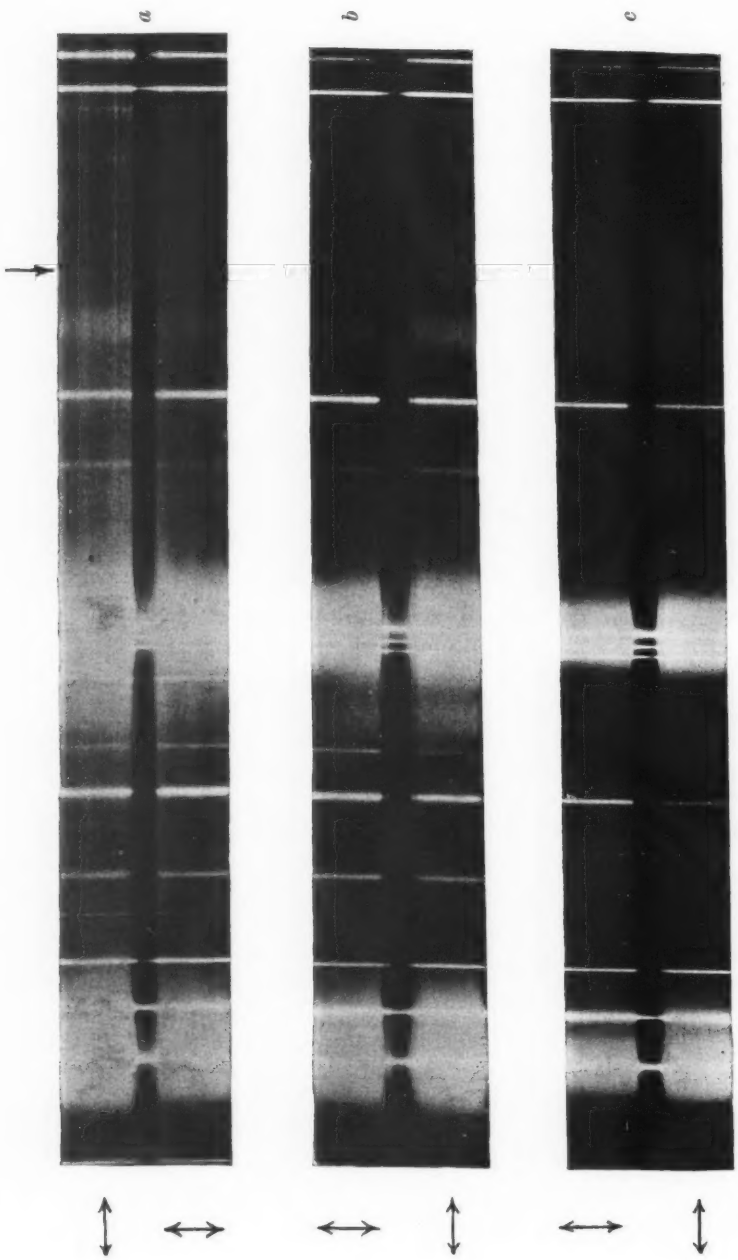
It is obviously of importance to obtain intense spectrograms, which are free from continuous spectrum, if all the features are to be studied in detail. In this investigation special efforts have been made in this direction and the pictures obtained with the nitrates of sodium, potassium and aluminium are reproduced in Plate III. As no data regarding the polarization characters of the lines are available in the early work already cited, these are obtained by the author. The clear wings recorded in the spectrograms permit of an accurate study of the intensity distribution in the

neighbourhood of the Rayleigh lines being made and some results obtained in this direction are also given. The first overtone of the fundamental oscillation at 880 of the NO_3 group is recorded in this paper and its characters studied for the first time in the molten nitrates. This has been rendered possible only by the very satisfactory experimental conditions that have been employed.

2. *Experimental Technique*

The substances used are Kahlbaum's chemicals further purified by repeated crystallisation from solutions. In the case of sodium and potassium nitrates, recrystallisation has been affected from saturated aqueous solutions whereas aluminium nitrate has been recrystallised from a solution containing excess of nitric acid, by precipitation method, after dissolving the sample in water. The substances are all dried thoroughly prior to their introduction into the containers. The container is a pyrex tube of $\frac{3}{4}''$ diameter flattened at one end and drawn out at the other into the shape of a horn, to which is attached a long neck. The tubes are all coated outside with black paint to avoid reflections with the exception of a region for illumination and another for observation.

For heating purposes, a cylindrical heater open at either end, of about 5 cm. diameter and 20 cm. length has been constructed. The heater is provided with a window 2×13 cm. in its body lengthwise for the purpose of illumination. The Raman tube is supported longitudinally inside the heater, by means of two discs with central apertures, which just fit into the heater. These discs serve not only as bridges to support the tube, but also to prevent the escape of heat from either end. One of the discs has a hole bored in it for the insertion of a thermometer as close to the tube as possible. Light from a $6''$ mercury arc is condensed by an $8''$ condenser on to the Raman tube through the window of the heater. The Raman tube is jammed against a small aperture in an asbestos sheet held in position. The scattered light is condensed on to the slit of a Hilger two-prism glass spectrograph of high light-gathering power. Between the lens and the aperture, a properly oriented double-image prism is introduced. The positions of the lens and the double-image prism are so adjusted as to form two distinctly separated images on the slit corresponding respectively to the horizontal and vertical components of the scattered light. With these arrangements it has been possible to see the 1050 $cm.^{-1}$ line visually through the instrument. An exposure of about $1\frac{1}{2}$ to 2 hours has been found sufficient to obtain clear and good spectra which are intense and quite free from continuous background. The depolarisation factors are determined in the usual manner



Raman Spectra of Fused Nitrates
a—Sodium ; *b*—Potassium ; *c*—Aluminium

by giving a set of intensity marks on the plate by the method of varying slit widths.

3. *Results*

In Plate III, Figs. *a*, *b* and *c* are the Raman spectra of fused sodium nitrate, potassium nitrate and aluminium nitrate respectively. In each case, the vertical and horizontal components are recorded side by side but simultaneously. The absence of continuous background, the presence of wings closely resembling those that are ordinarily met with in optically anisotropic liquids, the occurrence of the first overtone line (marked with an arrow) and the fact that this line is well polarised are among the noteworthy features that may be readily seen in the spectrograms. The considerable broadening exhibited by the band at 1400 may also be noted. The plates have been so well exposed that in some cases the anti-Stokes line corresponding to the principal oscillation at 1050 cm.$^{-1}$ has been recorded clearly although it is rather difficult to see the same in the reproductions.

The results in respect of polarisation characters obtained in the present investigation after making allowance for the several corrections are given below in Table I.

TABLE I

Frequency	700	1050	1400	1670
Mode	Degenerate	Symmetric	Degenerate	Overtone
($NaNO_3$)	0·8	0·2	0·8	0·5
(KNO_3)	0·9	0·3	0·8	0·5
$Al(NO_3)_3$	0·9	0·2	0·9	..

In the case of aluminium nitrate, at the place where the overtone is expected to appear, the water band has come out thus masking the overtone. This water band is due to the water of crystallisation of the aluminium nitrate molecule, $Al(NO_3)_3\ 9H_2O$ persisting as free water in the molten substance. Accordingly the depolarisation factor for the overtone in this case could not be obtained. The large degree of polarisation exhibited by the 1050 cm.$^{-1}$ line, the limiting values of depolarisation exhibited by 700 and 1400 cm.$^{-1}$ lines and the partial polarisation exhibited by the overtone are amongst the notable results in the table. These are in complete agreement with what may be expected theoretically.[18]

The distribution of intensity in the wing accompanying λ 4046 in fused sodium nitrate is determined and the results are given in Table II.

TABLE II

Intensity Distribution in the Wing in Fused $NaNO_3$

Wave number ..	13·5	27·0	40·5	54·0	67·5	81·0	94·5	108·0	121·5	135·0	148·5
Intensity ..	1245	372	195	155	138	127	115	112	107	102	80

The results are represented graphically in Fig. 1. It may be noted that the curve given in Fig. 1 possesses all the characters that are typical of the wing usually obtained in common liquids.

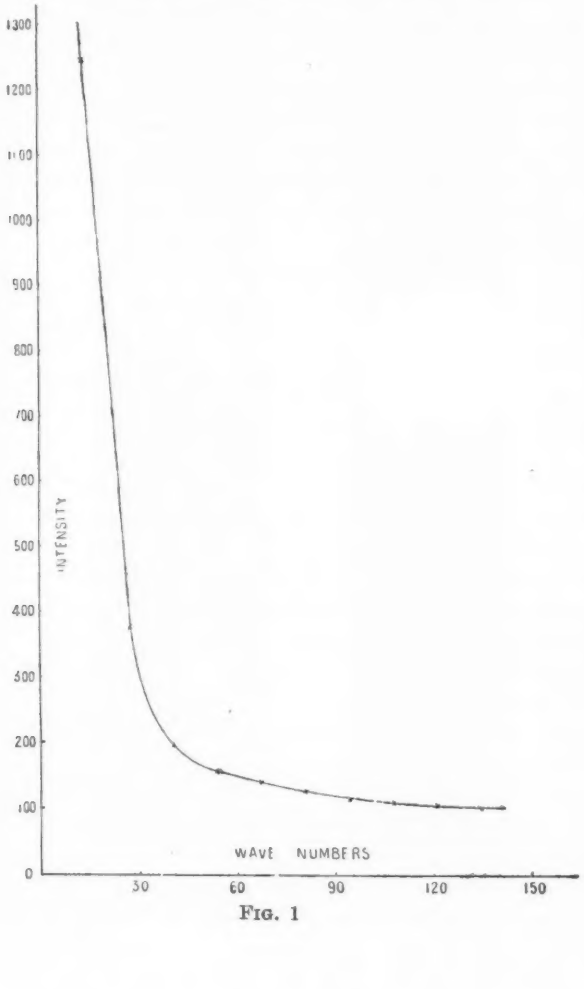


FIG. 1

Both the horizontal and vertical components of the wing are also microphotometered together with the intensity marks. At various points in the wing the intensities are calculated and the depolarisation at each point is obtained and the necessary corrections applied. The results are tabulated below in Table III.

TABLE III

Depolarisation Factor of the Wings : 100ρ

Wave number	7	14	21	28	35	42	49	56	63	70	77	84	91	98	105	112	119
$NaNO_3$ ..	74	87	105	100	108	109	116	109	115	107	103	86	86	89	98	81	79
KNO_3 ..	77	73	81	85	83	85	81	81	81	71	66						
$Al(NO_3)_3$ ..	60	94	103	108	116	111	116	116									

Except in the regions lying between 20 and 80 wave numbers in sodium and aluminium nitrates, the depolarisation factor is seen to be quite close to the theoretically expected value, namely 86%. It is not certain, if the comparatively high value obtained in the regions between 20 and 80 wave numbers is genuine. It is possible that small bits of crystals may have been floating in the molten liquid thus causing such a discrepancy. This point is a matter for further investigation and is being pursued by the author.

4. *Summary*

Clear and intense Raman spectra of fused sodium, potassium and aluminium nitrates have been obtained and reproduced in the paper. Each one of the spectra has been separated into the horizontal and vertical components by the use of a suitably oriented double-image prism. The depolarisation factors of the various Raman lines are given. The large degree of polarisation exhibited by the 1050 cm.$^{-1}$ line, corresponding to the symmetric expansion and contraction of the nitrate ion, the limiting value of depolarisation exhibited by the 700 and 1400 cm.$^{-1}$ lines corresponding to the two degenerate modes of oscillation of the NO_3 ion and the partial polarisation exhibited by the overtone line are amongst the noteworthy results. The overtone line (1660 cm.$^{-1}$) itself has been recorded for the first time in molten nitrates in the present investigation. The fact that it is a well polarised line is also a new result. The distribution of intensity within the wing accompanying the Rayleigh line λ 4046 in fused sodium nitrate has been studied. The wing starts with a maximum intensity at the centre and fades off in a manner which is very similar to that obtained in common liquids. Different portions of the wings in the nitrates studied

are found to be depolarised to the extent of 86% in agreement with what may be expected from theory.

In conclusion, the author desires to tender his most sincere thanks to Prof. S. Bhagavantam, under whose guidance this work has been carried out.

REFERENCES

1. Bär .. *Nature*, 1929, **124**, 692.
2. Krishnamurti .. *Ind. Jour. Phys.*, 1930, **5**, 1.
3. Schæffer, Mattossi and Aderhold *Zeit. f. Phys.*, 1930, **65**, 289.
4. Gerlach .. *Ann. d. Phys.*, 1930, **5**, 196.
5. Nisi .. *Proc. Phys. Math. Soc., Japan*, 1932, **14**, 214; 1933, **15**, 114.
6. Cabannes and Canals .. *Comptes Rendus*, 1931, **193**, 289; **196**, 977.
7. Rao .. *Zeit. f. Phys.*, 1934, **90**, 650; *Proc. Roy. Soc. London*, (A), 1934, **144**, 159.
8. Ananthakrishnan .. *Proc. Ind. Acad. Sci.*, 1937, **5**, 477.
9. Pattabhiramayya .. *Ibid.*, 1938, **7**, 229.
10. Nedungadi .. *Ibid.*, 1938, **7**, 397.
11. Carelli, Pringsheim and Rosen *Zeit. f. Phys.*, 1929, **51**, 511.
12. Woodward .. *Physikal. z.*, 1931, **32**, 777.
13. Ramaswamy .. *Ind. Jour. Phys.*, 1930, **5**, 193.
14. Kishi .. *Mem. Coll. Sci. Kyoto*, (A), 1930, **13**, 193.
15. Grassmann .. *Zeit. f. Phys.*, 1932, **77**, 616; 1933, **82**, 763.
16. Laird and Franklin .. *Phy. Rev.*, 1934, **45**, 738.
17. Thatte and Ganesan .. *Ind. Jour. Phys.*, 1933, **8**, 341.
18. Bhagavantam and Venkatarayudu *Proc. Ind. Acad. Sci.*, 1939, **8**, 235.

1. D. 1465—South-east view of Kailasanatha temple, Conjeevaram, Chingleput District

(Copyright—Archæological Survey of India)

2. D. 1472—North corridor from the east and main shrine, Kailasanatha temple, Conjeevaram, Chingleput District
The cells containing paintings are on the left lining the outer wall

(Copyright—Archæological Survey of India)

THE PALLAVA PAINTINGS AT CONJEEVARAM—AN INVESTIGATION INTO THE METHODS[1]

By S. Paramasivan

(*Archæological Chemist, Government Museum, Madras*)

Received August 1, 1939

I. Introduction

Conjeevaram (12° 51′ N. & 79° 43′ E.), the ancient Pallava capital, is situated 45 miles west-south-west of Madras on the South Indian Railway. It is rich in temples and shrines. Of them the most important are the Kailasanatha and the Vaikunṭhaperumal temples, which contain ancient wall paintings.

In the Kailasanatha temple, which was built during the time of the Pallava king, Narasimhavarman II *alias* Rajasimha (680–722 A.D.),[2] there are paintings of the 7th–8th centuries A.D. on the inner walls of the narrow cells lining the outer walls of the courtyard.[3] They depict scenes from Hindu mythology. But most of the paintings have faded or disappeared through the vicissitudes of time and elements. The few that have survived were covered with lime wash during recent times. But Prof. Jouveau Dubreuil, the French archæologist of Pondicherry, removed the layer of white wash here and there and brought the paintings to light.

Nandivarman II *alias* Pallavamalla (725–790 A.D.)[2] constructed the Vaikunṭhaperumal temple. The paintings in this temple, probably dating from the 8th–9th centuries A.D., have almost disappeared but for a miniature head under one of the eaves of the central tower or the *Vimāna*. But there are traces of paint everywhere under the eaves and in the niches (*kŭdus*) of the central tower.

These Pallava paintings are on the classical or Ajanta style, and represent some of the best specimens of Hindu mural art.

II. Experimental Investigations

In order to reconstruct the methods and materials used in these paintings, one has to study and experiment on the *carrier*, the *ground*, the *pigments* and the *binding medium*.[4] Investigations were carried out on some damaged fragments of the *painted stuccoes* which were collected from the two temples.* The *painted stuccoes* consisted of *rough plaster* of lime, which had been applied to the wall, with two successive coats of *fine plaster* and of paint applied one over the other. Some of the *stuccoes* in the Kailasanatha

* The author is indebted to Mr. T. N. Ramachandran of the Archæological Survey of India for his help.

temple were very thin. They had no *rough plaster*, being made up of a layer of lime wash or *fine plaster* supporting the layer of paint. The methods of production of the paintings in the two temples are so similar, that a common discussion of their experimental results will suffice.

(1) *The Carrier.*

The inner walls of the cells in the courtyard of the Kailasanatha temple, and the eaves and the walls of the niches (*kūdus*) of the *vimāna* of the Vaikunṭhaperumal temple serve as the mechanical foundation of the paintings directly supporting the *ground*. They are of sandstone, which are mechanically firm and durable. Their rough surface holds the plaster fast.[5] Their material, being hard and compact, eliminates any possibility of efflorescence occurring on the surface of the paintings.[6] In the Vaikunṭhaperumal temple, the *ground* and the *paint* have fallen down in several places. The *carrier* has thus become exposed to the elements resulting in further damage to the paintings.

(2) *The Ground.*

In order to determine how the *ground* was prepared and what materials had been used in it, the following experiments were carried out :—

Study of the Microsection. Microsections of the painted stuccoes showing all the different layers composing them, were prepared.[7] On examining them under the microscope, they showed two lines of cleavage or junctions separating three distinct layers, namely, of (1) the *rough plaster*, (ii) the *fine plaster* and (iii) the *paint*. It was possible to effect a separation between the layers of paint and the *fine plaster* with a sharp pin. But it was very difficult to separate the *fine plaster* from the *rough plaster*. In a few places, such separation could be effected with ease. The significance of these results will be discussed later.

The thicknesses of the different layers of the painted stuccoes were as follows :

	Kailasanatha temple mm.	Vaikunṭhaperumal temple mm.
Painted Stucco ..	2·1–4·3	3·4–4·7
Rough Plaster ..	1·5–3·7	2·8–4·1
Fine Plaster ..	0·3	0·3
Paint film ..	0·3	0·3

3. D. 1780 to 1780 (*c*)—Mutilated painting showing Somaskanda with two attendants in a niche on the north corridor, Kailasanatha temple, Conjeevaram, Chingleput District

(Copyright—Archæological Survey of India)

The *rough plaster* in the Kailasanatha temple is relatively thinner than in the Vaikuṇṭhaperumal temple.

Size of Particles in the Rough Plaster.—The *rough plaster* was completely separated from the *fine plaster*. The particles composing it were mechanically separated by Robinson's method[8] and graded according to size. The sizes of the particles and their proportions were as follows :—

	< 200 μ	200 μ–700 μ	> 700 μ
Kailasanatha (*Rough Plaster*) ..	29%	57%	14%
Vaikuṇṭhaperumal (*Rough Plaster*) ..	29%	57%	14%

Particles less than 200 μ were composed of lime, clay and finer particles of silica. The larger particles were mostly of silica.

Analysis of the Plaster.—In order to ascertain how the *ground* was prepared for supporting the paintings, a few samples of the *rough plaster* completely freed of the *fine plaster* and samples of *fine plaster* completely freed of the *rough plaster* and the paint film, were analysed. The results of chemical analyses of representative specimens of the *rough plaster* were as follows :

	Kailasanatha temple (Per cent.)	Vaikuṇṭhaperumal temple (Per cent.)
Moisture	1·08	0·17
Carbon dioxide, CO_2	9·45	21·52
Combined water and Organic matter ..	5·66	2·66
Silica, SiO_2	65·37	46·63
Iron and alumina, $Fe_2O_3 + Al_2O_3$ ..	2·06	1·97
Lime, CaO	15·71	26·73
Sulphuric Anhydride, SO_3	nil	0·15
Magnesia, MgO	nil	0·04
Undetermined (Mostly alkalies) ..	0·67	0·13
TOTAL ..	100·00	100·00

The samples of *fine plaster* were treated with dilute hydrochloric acid. They disintegrated, dissolved with effervescence and evolution of carbon dioxide, and left behind a residue of fine particles of silica. The acid solution gave tests only for calcium. Thus the fine plaster consists of lime wash.

The results of analyses of the *rough plaster* show that the principal components of the rough plaster are lime and sand, which have brought about the consolidation[9] of the plaster. Here sand serves merely as an

SOMASKANDA
(Blocks lent by Mr. C. Sivaramamurti)

inert material.[10] The rough plaster has been given a coat of lime wash and probably trowelled over to impart smoothness and gloss to the surface.[11] Hence the *ground* has been prepared out of *rough plaster* of lime and covered with lime wash.

The percentage of iron and alumina in the *rough plaster* is very low. It indicates that a pure rich lime having no hydraulic properties has been

used. Gypsum prevents the setting of the plaster in which it might be present and gives rise to efflorescence on the surface of the paintings. Its amount can be gauged from the percentage of sulphuric anhydride, in the results of analysis. But there is no sulphuric anhydride in the Kailasanatha plaster and the proportion of it in the Vaikuṇṭhaperumal plaster is negligible. The low percentage of impurities such as alkalies and other

MAHAPURUSHA
(Blocks lent by Mr. C. Sivaramamurti)

soluble salts, of iron and alumina and of gypsum, the firm adherence of the plaster, the absence of slaking on the *ground* and the fine gloss of the lime wash indicate that some sort of pit lime or specially prepared lime was used.[12] From the good preservation of these paintings it is evident that the Pallava artists have taken the usual precautions against the wetness of sand and open storage of lime.[13]

The *rough plaster* is very thin and varies from 1·5 mm. to 3·7 mm. in the Kailasanatha temple and from 2·8 mm. to 4·1 mm. in the Vaikuṇṭhaperumal temple. Particles of the *rough plaster* taken at different depths from the surface of the paintings showed diminishing percentages of carbon dioxide content. In other words, the *ground* is so very thin that carbon dioxide should have penetrated from the surface to the back.

Inert Materials in the Plaster.—The results of chemical analysis show that sand alone has been added as inert material in the plaster. But if the artists had added marble dust as in ancient Italy[14] or powdered shell or

limestone—the original materials from which the lime might have been prepared, and which give the same reaction as carbonated lime—they would not have been made known in the course of chemical analyses. But density measurements and microscopic examination[15] of the particles of the *rough plaster* and the *fine plaster* indicated that none of them had been added.

The sand grains which serve as the inert material in plaster looked sharp and angular under the microscope and they had contributed to the firmness of the plaster.[16]

Technique of laying the ground.—The percentage of water and organic matter in the Kailasanatha and Vaikuṇṭhaperumal plasters are 5·66 and 2·66 respectively. The next problem is to determine whether this includes any organic binding medium originally added to the plaster to consolidate it. The *rough plaster* was hard, stood prolonged soaking in cold and boiling water, and hence had no organic water-soluble binding medium in it. Methylene blue, methyl violet, acid green and iodoeosin did not leave any stain[17] on the plaster. Thus the plaster did not contain drying oil, glue, albumin or casein as binding medium. Nor did the plaster give Molisch's tests with α-naphthol. Thus there was no gum present. On treatment with dilute hydrochloric acid, the fragment of the plaster disintegrated with evolution of carbon dioxide and separation of silica, the solution giving tests for calcium. Thus lime alone has brought about the consolidation of the plaster. The same is true of the *fine plaster*.

Method of laying the ground.—Thus it will be clear that the artists applied the first coat of *rough plaster* to a thickness varying from 1·5 mm. to 3·7 mm. in the Kailasanatha temple and from 2·8 mm. to 4·1 mm. in the Vaikuṇṭhaperumal temple depending upon the inequalities of the surface of the *carrier*. Over the *rough plaster* was laid a thin coat of lime wash to a thickness of 0·3 mm. and probably trowelled over to impart a smoothness to the surface. Since the latter was applied while the former was still wet, the binding has been very strong and it was difficult to separate the two layers. Wherever the layer of lime wash could be easily separated from the *rough plaster*, the former should have been applied after the latter had dried. It should be mentioned here that in certain places in the Kailasanatha temple, there is no *rough* plaster, but that the *ground* consists mainly of lime wash.

(3) *The Pigments.*

The following pigments were identified[18] in the Kailasanatha and Vaikuṇṭhaperumal temples :—

Yellow ochre
Red ochre

Terre verte
Carbon
Lime

Thus only a limited number of pigments have been employed by the Pallava artists. This might be due to two causes. Firstly, in the fresco process such as is adopted here—and this will be proved presently—pigments which are sensitive to alkalies should not be used with lime. Secondly, the artists might have employed the locally available pigments, which were probably few in number.

(4) *The Binding Medium.*

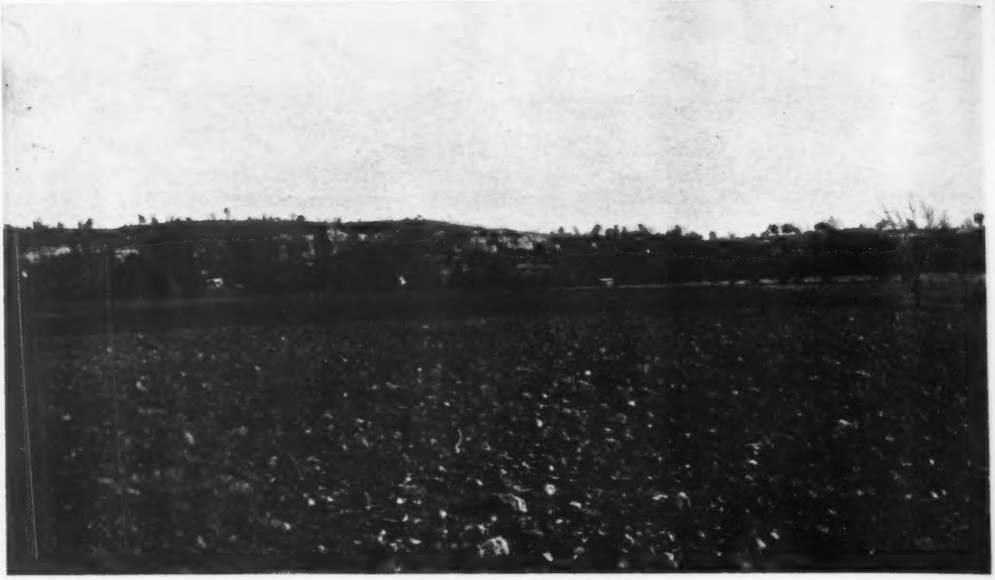
The paint layer is fairly adhering to the *ground*. The painted surface could be brushed without any damage occurring to it. It stood prolonged soaking in cold and boiling water. Thus there was no water-soluble binding medium in the paint. Methylene blue, methyl violet, acid green or iodoeosin left no stain[19] on the paint film. Thus there was no drying oil, glue, albumin, or casein as the binding medium in the paint. At the same time no vehicle could be extracted with ether, chloroform or carbon disulphide. Under the action of dilute hydrochloric acid a fragment of the paint film disintegrated completely with effervescence and evolution of carbon dioxide, the acid solution giving tests for calcium. Thus only lime has bound the pigments to the *ground*. Since the pigments have not interfused[20] in the plaster *ground* and spread beneath the *stucco* surface, the technique employed is one of *lime medium*. This is also confirmed by the absence of brush marks on the *ground*.[21]

Black wets poorly and a little glue or gum must be added to it before grinding.[22] It has already been shown that the paint film gave no reaction for organic binding medium and that the technique employed in laying them is one of *lime medium*. But the black paint, quite unlike others, answers Molisch's test, giving a violet ring with α-naphthol, which is a characteristic reaction for carbohydrates including gum. At the same time, lime water should have been used in mixing up the pigment to impart to the paintings the characteristics of *lime medium*.

Since the pigments have been laid in *lime medium*, it is not easy to note the extent of the ground that was covered in the course of a single day from an examination of the joinings from day to day's work.[23] Joinings in the plaster are more easily visible in *true fresco* technique than in *lime medium*. Further the coloured background and the considerable damages to which the paintings have been subjected render it impossible to perceive such joinings.

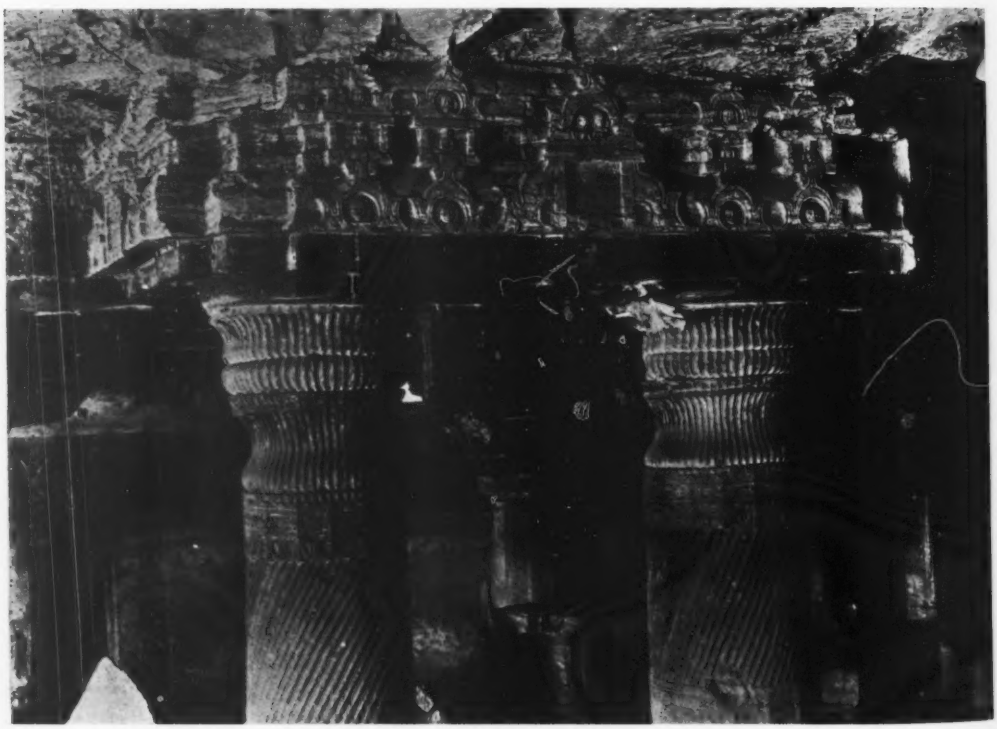
REFERENCES

1. *Nature*, 1938, **142**, 757.
2. C. Minakshi, " Administration and Social Life under the Pallavas " (Madras University), 1938, p. 117.
   N. Venkataramanayya, " The Date of Nandivarman Pallavamalla, " *Jour. Ori. Research*, **8**, p. 1*ff*.
   For other dates, *vide* Prof. Jouveau Dubreuil, Ancient History of the Deccan, (Pondicherry : Modern Press), 1920, p. 70.
3. "A Discovery of Some Ancient Paintings of Southern India," *The Students' Own Magazine*, Calve College, (Pondicherry: 1931, **1**, No. 2).
   T. N. Ramachandran, " The Royal Artist Mahendravarman I, " (Reprinted from *the Journal of Oriental Research*, Madras), pp. 27–28.
   C. Sivaramamurti, " Paintings from the Kailasanatha Temple, " *Jour. Ori. Research*, Madras, (1938), **11**, pp. 73–76.
4. Daniel V. Thompson, " The Materials of Medieval Painting " (Yale University Press : New Haven), 1936, pp. 43–47.
5. ————, *Loc. cit.*, p. 39.
6. S. Paramasivan, " The Mural Paintings in the Brihadisvara Temple at Tanjore– An Investigation into the Method," *Technical Studies* (Harvard), 1936–37, **5**, 224.
7. ————, " Technique of the Painting Process in the Temple of Vijayalaya Cholisvaram in the Pudukkottai State," *Proc. Ind. Acad. Sci.*, 1938, **7**, p. 284.
8. Norman G. Comber, "An Introduction to the Scientific Study of the Soil" (Arnold), 1927, pp. 48–49.
   G. W. Robinson, " Soils : Their Origin, Constitution and Classification" (Murby), 1932, pp. 12–13.
9. J. W. Mellor, " A Comprehensive Treatise on Inorganic and Theoretial Chemistry (Longmans, Green & Company, 1923), **3**, 677.
10. *Proc. Ind. Acad. Sci.*, **7**, 286.
11. *Loc. cit.*, p. 288.
12. Max Dœrner, "The Materials of the Artist and their Use in Painting," translated. (New York : Harcourt, Brace & Company), 1934, p. 269.
13. *Technical Studies* (Harvard), 1936–37, **5**, p. 231.
14. A. P. Laurie, Greek and Roman Painting (Cambridge University Press), 1910, p. 75–86.
15. *Proc. Ind. Acad. Sci.*, 1938, **7**, 286–87.
16. *Technical Studies* (Harvard), 1936–37, **5**, 230–31.
17. William Ostwald, "Iconoscopic Studies (Microscopic Identification of Homogeneous Binding Mediums) translated," *Technical Studies*, 1935–36, **4**, pp. 135–44.
18. Martin de Wild, The Scientific Examination of Pictures, (London : G. Bell & Sons, Ltd)., 1929.
    R. G. Gettens and G. L. Stout, " The Stage Microscope in the Routine Examination of Paintings," *Technical Studies* (Harvard), 1936–37, **4**, 224–28.
19. William Ostwald, *Loc. cit.*
20. Mary Hamilton Swindler, Ancient Painting (New Haven : Yale University Press), 1929, p. 418.
21. *Technical Studies* (Harvard University), 1936–37, **5**, p. 234.
22. *Loc. cit.*, p. 233.
23. *Loc. cit.*, pp. 237–240.



1. Bagh Caves. General View

(With the kind permission of the Director of Archæology, Gwalior State)



2. Cave No. 4 at Bagh, Interior. A Frieze

(With the kind permission of the Director of Archæology, Gwalior State)

THE WALL PAINTINGS IN THE BAGH CAVES—AN INVESTIGATION INTO THEIR METHODS

By S. Paramasivan

(Archæological Chemist, Government Museum, Madras)

Received August, 1, 1939

I. Introduction

The Bagh caves (22° 22′ N. & 74° 48′ E.) contain some of the finest examples of Indian wall paintings. Mutilated and faded as these paintings are, they still constitute a priceless treasure comparable to those at Ajanta. They have attracted considerable attention.[1]

The caves, which are nine in number, are situated on the southern slopes of the Vindhya hills in the Amjhera District of the Gwalior State. They are 70 miles from Mhow, the nearest Railway station, on the Rajputana-Malwa section of the B. B. & C. I. Railway. The cliff side on which the caves are excavated rises to a height of about 150 feet above the Bagh river and is remarkable as being only the outcrop of sandstone in an otherwise basaltic region. These sandstone caves are surmounted by a deep band of claystone.

The interior of these caves was at one time fully decorated with paintings. But the caves have crumbled due to the excessive weight of the superimposed band of claystone. Moisture percolating through it has also contributed to their destruction. Thus, with the crumbling of the caves many of the paintings have disappeared except a few in caves III and IV.[2]

The paintings probably date from the early seventh century A.D., being contemporaneous with the paintings in caves XVI and XVII at Ajanta.[3]

The paintings of Bagh and Ajanta form a distinct class by themselves, and belong to the golden age of Indian classical art, which inspired more than half the art of Asia.* They will bear comparison with the best that Europe could produce down to the time of Michael Angelo.[4]

---

* "As far as their artistry is concerned, there is little to choose between the pictures of Bagh and Ajanta. Both exhibit the same broad handling of their subjects, the same poetry of motion, the same wonderful diversity in the poses of their figures, the same feeling for colour and the same strong yet subtle line-work. In both, decorative beauty

II. Experimental Investigations

In reconstructing the technique of the painting process adopted by the ancient classical artists at Bagh, one has to consider the four principal factors[5] that go to make up the paintings. They will be considered here in order. Samples of three kinds of *painted stuccoes* that were available were collected from damaged portions of the paintings in cave IV at Bagh, and experiments conducted with them. Two of them had *rough plaster* of deep red and light red ferruginous earth, while the third had *rough plaster* of lime. Over them was a layer of *fine plaster* of some white material, the latter supporting the painted layer.

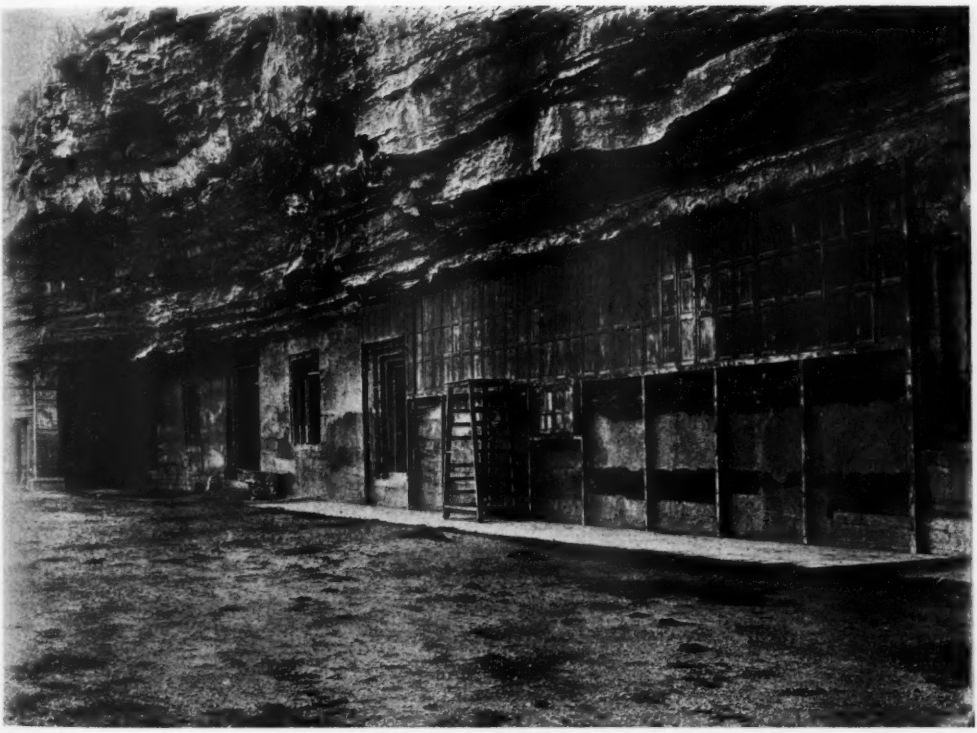
(1) *The Carrier.*

The walls of the cave temples, and probably also its ceilings, serve as the mechnical supports for the paintings, and function as the *carriers*. They are of sandstone. The surface of the *carrier* has been specially left rough so that the *rough plaster* might hold well.[6] The sandstone caves were unable to support the excessive weight of the superimposed band of claystone. Consequently, the walls and ceilings, which are otherwise fairly firm and compact, have crumbled and fallen to pieces, thus destroying the paintings. Moisture has been percolating into the cave from the top, and it has softened and damaged the earth plaster and the paintings attached to them. In several samples, the paintings are covered with white efflorescence caused by the presence of gypsum, sodium sulphate, magnesium sulphate, etc. The efflorescence can be traced to salts carried over by the percolating water from outside and deposited over the surface of the paintings, and not to the presence of salts in the plaster (*vide* results of analysis below).

---

is the key-note to which all else is attuned, and both are as free from realism as they are from stereotyped convention. The artists, to be sure, have portrayed their subjects direct from life—of that there can be no doubt, but however fresh and vital their portrayal may be, it never misses that quality of abstraction which is indispensable to mural decoration, as it is, indeed, to all truly great painting. True, there is nothing left at Bagh to equal some of the surprisingly majestic figures, such as the famous Bodhisattva, at Ajanta, but in one respect at any rate the paintings of Bagh have an advantage over those of Ajanta. For whereas at Ajanta most of the paintings appear to have been done piecemeal—at Bagh they give the impression of having been conceived and executed at one and the same time, or at any rate in conformity with a single well-thought out scheme....To be adequately appreciated they (the paintings) must be seen to their full scale and in the architectural setting for which they were designed."—SIR JOHN MARSHALL.

Vide Sir John Marshall & others, *The Bagh Caves* (London: India Society), 1927, pp. 17–18.



3. Cave No. 4 at Bagh, Facade (Frescoes are inside the shutters)

(With the kind permission of the Director of Archæology, Gwalior State)

(2) *The Ground.*

The following experiments were conducted to study the nature of the *ground* which had been prepared by the Bagh artists to lay the coloured designs on.

Study of the microsection.—Microsections of the *painted stuccoes* containing all the different layers were prepared.[7] Since the earth *stuccoes* were very soft, considerable care was bestowed in preparing them. Particles of dust adhering to the prepared surface were removed very carefully with a soft brush. An examination of the surface under the travelling microscope revealed three lines of cleavage† or junctions in the case of the earth *stuccoes* and two in the case of the lime *stucco* thus showing the presence of four and three distinct layers respectively in them. They consisted of the top layer of paint with a layer of some white material serving as *fine plaster* just underneath, with two layers of *rough plaster* in the case of the earth *stuccoes* and one layer in the case of lime stucco. The thicknesses of the different layers were as follows :

	Earth Stuccoes		Lime Stucco
	Deep red	Light red	
	mm.	mm.	mm.
Painted Stucco ..	8–20·2	8·1–20·2	3·8–6·9
Rough Plaster— First layer ..	6·8–19·9	6·9–19·0	3·4–6·5
Second layer ..	1·0	1·0	
Fine Plaster ..	0·1	0·1	0·2
Paint Film ..	0·1	0·1	0·2
Average thickness of of the painted stucco	17·2	17·2	4·9

† On account of the softness of the *earth stucco* it was difficult to separate the different layers along the junctions. In the case of the *lime stucco*, such separation could be effected with greater ease.

The earth *stuccoes* are very much thicker than the lime ones. The paint film in the *lime stuccoes* is twice as thick as that on the earth *stuccoes*. In other words, the paint film on the *lime stucco* shows a certain lack of delicacy in the artists' handling of the brush. It is, therefore, probable that the *lime stucco* does not belong to the palmy days of Bagh, or that the paintings on the earth and lime stuccoes were done by different groups of artists.

Size of the Particles in the Plaster.—The rough plaster was carefully separated from the layer of *fine plaster* and the layer of paint film and gently crushed between fingers so as to avoid breaking the larger particles into smaller ones. The particles composing it were mechanically separated and graded according to size by Robinson's method.[8] The proportion and sizes of the particles were as follows :—

	< 200 μ (Per cent.)	200 μ–700 μ (Per cent.)	>700 μ (Per cent.)
Earth Plaster : Bright red ..	17	50	33
Light Red ..	20	40	40
Lime Plaster ..	60	40	nil

In the case of the earth plaster, particles smaller than 200 μ are mostly composed of laterite, silica and clay, while the larger particles are mostly of sand and laterite. In the case of the lime plaster, particles smaller than 200 μ are composed of lime, clay and sand, while the larger particles are mostly composed of sand.

The sand grains and particles of laterite are larger in size in the *rough plaster* than in the *fine plaster*, the latter containing minute particles whose diameters vary from 14 μ to 28 μ. The use of coarse sand grains for the underlayers and finer ones for the top is recommended by artists in the West.[9]

Analysis of the Plaster.—In order to determine the method originally employed by the Bagh artists for preparing the *rough plaster*, its chemical composition was ascertained, the results of analyses of representative specimens being as follows :—

	Earth Plaster		Lime
	Deep Red (Per cent.)	Light Red (Per cent.)	Plaster (Per cent.)
Moisture	0·27	0·42	0·91
Carbon dioxide, CO_2	1·25	0·65	12·68
Combined Water and Organic Matter	0·55	1·03	9·34
Silica, SiO_2	87·22	87·10	51·18
Iron, Fe_2O_3	6·12	3·11	2·23*
Alumina, Al_2O_3	0·44	5·29	
Phosphoric Acid, P_2O_5 ..	0·12	0·10	
Titanic Acid, TiO_2	0·09	0·07	
Lime, CaO	2·11	0·75	22·41
Magnesia, MgO	0·56	0·44	..
Manganese, Mn_3O_4	0·75	0·39	..
Sulphuric Anhydride, SO_3 ..	..	..	0·04
Alkalies	0·44	0·62	1·21
Nitrogen	0·13	0·09	..
TOTAL ..	100·05	100·06	100·00

* Only iron and alumina predominate, phosphoric acid and titanic acid occurring in negligible quantities.

Some of the scrapings of the *fine plaster* were completely freed from the paint film and the rough plaster. On treating them with dilute hydrochloric acid, they dissolved with effervescence and evolution of carbon dioxide with the separation of fine particles of silica. The acid solution gave reactions for calcium and for a sulphate, the latter occurring only in relatively small proportions. Thus the *fine plaster* was a mixture of lime and calcium sulphate which had been applied to the surface of the *rough plaster* to serve

as *fine plaster*.[10*] In the lime stucco, the *fine plaster* was composed of lime alone without any trace of calcium sulphate. Since it was impossible to get samples of the *fine plaster*, unaccompanied by *rough plaster*, the proportion of lime and calcium sulphate was not determined.

Thus the *ground* was prepared out of naturally occurring ferruginous earth or of artificially prepared lime plaster. The principal components of the earth plasters are silica, iron, alumina and lime. In the case of the lime plaster, the principal components are lime and silica.

The proportions of silica in the earth plasters are almost identical, while their colour seems to have been influenced by the proportion of iron. The proportion of lime present in the earth plasters is too low to have been purposely added to the original material. Hence it should have been present in the original materials as an impurity. The earth plasters are fairly firm and strong.† It will be shown below that the *rough plasters* do not contain any organic binding medium. Hence the consolidation of the earth plaster may be attributed to the plasticity of clay[11] present in it, and this is evident from the proportion of iron and alumina. In the case of the lime plaster, lime and sand contribute to the firmness and strength of the plaster.[12] The plasters have also been reinforced and bound with vegetable fibres,[13] the lime plaster containing considerable quantities of them.

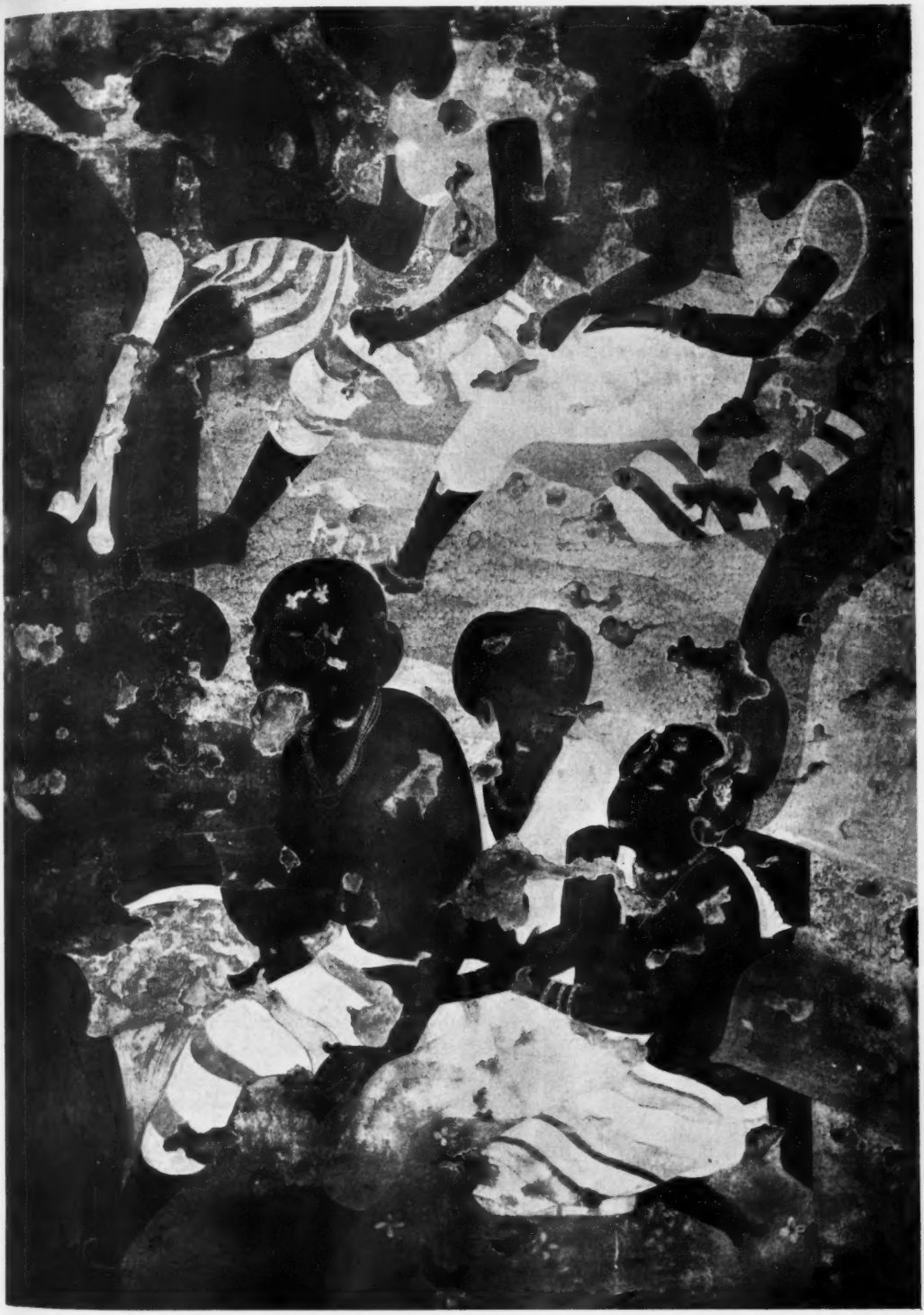
The percentage of alkalies and sulphuric anhydride in the earth plasters is low. In other words, presence of soluble salts and of gypsum which gives rise to efflorescence on the surface of the paintings can be ignored. The other impurities in the earth plasters are not of much significance in reconstructing the technique of the painting process or in affecting the permanence of the paintings.

From the small proportion of iron and alumina in the lime plaster, it is clear that the percentage of clay in it is very low. Thus a pure rich lime having no hydraulic properties has been used. From the low percentage of sulphuric anhydride, one can ignore the presence of gypsum, which

---

* *Fine plaster* of gypsum has been used in the wall paintings of Bamiyan in Afghanistan and Kizil in Chinese Turkestan, which had cultural contact with India.

† In *The Bagh Caves* (London: India Society), 1927, pp. 16–17, Sir John Russel remarks that, "the rinzaffo is less tenacious than at Ajanta—a fact that has contributed in no small measure to the deterioration of the paintings." This is to be attributed to the larger proportion of clay in the Ajanta plaster than in the Bagh ones. Further, the Ajanta plaster has a larger proportion of vegetable fibres in it than the Bagh plaster has. This has also contributed to the better consolidation of the Ajanta plaster.



4. Cave No. 4 at Bagh, fresco-painting. A part of an elephant procession

(With the kind permission of the Director of Archæology, Gwalior State)

prevents the setting of mortar and causes efflorescence to appear on the surface of the paintings. The small proportion of impurities such as alkalies and other soluble salts, the firm adherence of the plaster and the absence of slaking on the *ground* indicate that special attention should have been paid to the preparation of lime.[14]

Inert Materials in the Plaster.—Since the consolidation of the earth plasters is due to the plasticity of clay present in it, silica, iron, manganese and lime (present as the carbonate) are the inert materials. Silica alone occurs to the extent of 87%. In the case of lime plaster, the results of chemical analyses show that sand alone is the inert material, for a pure rich lime without the admixture of an inert material would not have yielded a satisfactory plaster.[15] But further experiments[16] conducted show that marble dust (which was invariably used with the Italian frescoes and which give the same chemical reactions as carbonated lime) is not present in the plaster. But the plaster contained particles with density 2·72[16]. The silica present in the plaster was associated with hydrated yellow oxide and anhydrous red oxide of iron, thereby showing that unburnt limestone has been added to the lime for preparing the plaster or that partially burnt limestone has been used for the purpose.[16] The sand grains serving as the inert materials looked sharp and angular and have contributed to the firmness and strength of the plaster.[17]

Technique of laying the ground.—The percentages of combined water and organic matter in the two earth plasters and in the lime plaster are 0·55, 1·03 and 9·34 respectively. That this is not due to the presence of any organic binding medium like drying oil, glue, albumin or casein is proved by the absence of any stain[18] when the plaster is acted upon by methylene blue, methyl violet, acid green or iodoeosin. Thus the organic matter present in the plaster must be the vegetable fibres and some organic impurities. In the case of the *rough plaster* of lime, a sample of it softened considerably under the action of water. On treating it with dilute hydrochloric acid, it disintegrated with evolution of carbon dioxide and separation of silica, the acid solution giving tests only for calcium. Thus the lime plaster has been composed of a mixture of burnt and unburnt limestone or of limestone partially burnt, and hence lacking in consolidation. The approximate probable composition of the limestone used for the preparation of the plaster seems to be as follows :—

	(Per cent.)
Calcium carbonate, $CaCO_3$ ..	44·17
Silica, SiO_2	53·30
Iron and Alumina, $Fe_2O_3 + Al_2O_2$	2·45
Calcium sulphate, $CaSO_4$ ..	0·08
TOTAL ..	100·00

The *fine plaster* did not soften when acted upon by water. Otherwise its behaviour towards staining agents and dilute hydrochloric acid was exactly similar to that of the *rough plaster* of lime. Thus lime has brought about the consolidation of the *fine plaster*.

Method of laying the ground.—From experimental results it is clear that the artists applied the first coat of earth plaster or of lime plaster containing vegetable fibres. The former received a second coat of rough plaster of earth to a thickness of 1 mm. The total thickness of the *rough plaster* varied from about 7·8 mm. to 20 mm. and from 3·4 mm. to 6·5 mm. respectively depending upon the inequalities of the surface of the *carrier*. While the ferruginous earth was naturally occurring, the lime plaster had been prepared either by mixing burnt and unburnt limestone or by partially burning the limestone, and preparing the plaster out of it. The *rough plaster* has been given a coat of *fine plaster* containing a mixture of lime and calcium sulphate in the case of the earth plaster and of lime alone in the case of lime plaster and the surface smoothened.

(3) *The Pigments.*

The following pigments were identified[19] in the paintings at Bagh :—

Yellow ochre.
Red ochre.
Terre verte.
Lapis lazuli.
Carbon.
Lime.

Over the lime plaster, the pigments that were identified were the yellow and red ochres, carbon and lime. Thus the colour scale is very limited. Evidently only those colours which were easily available locally were employed.

(4) *The Binding Medium.*

The paint film is fairly adhering to the plaster. It easily disintegrates when soaked in cold and boiling water and no gum could be extracted with

water from it. No vehicle or organic binding medium could be extracted from the paint film with ether, carbon disulphide and chloroform used separately and successively. There was no stain on the paint film when it was acted upon by methylene blue and methyl violet, but acid green stained the paint film thereby showing the presence of glue as a binding medium.[18] When a small particle of the paint film was covered with a drop of water, a glue ring with characteristic glue crackle formed on evaporation of the water.[20] Thus a *tempera* technique had been employed in the execution of the paintings. With a few samples of the earth stucco, no stain was developed on the paint film either with acid green or iodoeosin. On treatment with dilute hydrochloric acid, such paint films disintegrated with evolution of carbon dioxide, the acid solution giving tests for calcium. This reaction was characteristic of the paint film on all the samples of lime plaster collected. But the pigments had not interfused or spread beneath the plaster *ground*, and hence the technique is one of *lime medium*.[21] This is to be expected for the layer of lime on the earth plaster is too very thin for the *ground* to remain wet for sufficient time for *true fresco* process to be adopted. In the case of the lime stucco, the *rough plaster* has not well consolidated on account of the poor quality of the lime which is mostly unburnt while, for the *true fresco* process, well burnt and well slaked lime is used.[22] The *fine plaster* on the *rough plaster* is too thin to retain any moisture for any considerable time for the paintings to be done in the *true fresco* style.

Black wets poorly and a little gum or glue must be added to it before grinding.[23] A sample of the black paint gives the usual stain for glue with acid green.[18]

Since the paintings have been done either in *tempera* or in *lime medium*, it is very difficult to say the extent of the *ground* that was covered in the course of a single day from a detailed examination of the joinings of day-to-day's work.[24] Joints in the plaster are more easily visible in *true fresco* than in *lime medium*. Further colours employed for the background makes it difficult to detect any joint.

In conclusion, the author wishes to express his thanks to Mr. M. B. Garde, Director of Archæology of the Gwalior State, who took the trouble to collect the samples of *painted stuccoes* on which investigation were carried out, and for his generous help, to Mr. J. F. Blakiston, formerly Director-General of Archæology in India and to Rao Bahadur K. N. Dikshit, Director-General of Archæology in India, for their great interest in the subject.

REFERENCES

1. *Transactions of the Literary Society of Bombay*, **2**, 206–14.
2. *Journal of the Bombay Branch of the Royal Asiatic Society*, **4**, 543–573.
   Indian Antiquary, **39**, 225.

Sir John Marshall and others — *The Bagh Caves in the Gwalior State* (London : India Society), 1927.

Burgess, J. .. — *Notes on Bauddha Rock Temples of Ajanta, their Paintings and Sculptures and on the Paintings of the Bagh Caves* (Bombay Government Central Press), 1879, 94–95.

Benjamin Rowland and others — *The Wall Paintings of India, Central Asia and Ceylon* (Boston : Merrymount Press), 1938, pp. 79–81.

———— .. — *Loc. cit.*, pp. 79–81.

3. Sir John Marshall and others — *Loc. cit.*, p. 22.
4. ———— .. — *Loc. cit.*, p. 5.
5. Daniel V. Thompson .. — *The Materials of Medieval Painting* (New Haven : Yale University Press), 1936, pp. 43–47.
6. ———— .. — *Loc. cit.*, p. 39.
7. S. Paramasivan .. — " Technique of the Painting Process in the Temple of Vijayalaya Cholisvaram in the Pudukkottai State," *Proc. Ind. Acad. Sci.*, 1938, **7**, 284.
8. Norman G. Comber .. — *An Introduction to the Scientific Study of the Soil* (London : Arnold), 1927, 48–49.

G. W. Robinson .. — *Soils : Their Origin, Constitution and Classification* (London : Murby), 1932, 12–13.

9. A. P. Laurie .. — *The Painter's Methods and Materials* (London : Seeley & Co.), 1926, 197.
10. Rutherford, J. Gettens.. — " The Materials in the Wall Paintings of Bamiyan," *Technical Studies*, 1938, **6**, 186.

———— .. — " The Materials in the Wall Paintings from Kizil in Chinese Turkestan," *Technical Studies*, 1938, **6**, 283.

11. Searle .. — *The Chemistry and Physics of Clays and other Ceramic Materials* (London : Ernest Benn), 1924, 262–63.
12. J. W. Mellor .. — *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (London : Longmans, Green & Co., 1923, **3**, 677.
13. .. — *Encyclopædia Britannica*, 14th Edition, **18**, 39–40.
14. Max Doerner .. — *The Materials of the Artist and their use in Painting*, translated (New York : Harcourt, Brace & Co.), 1934, 269.

15. S. Paramasivan .. *Loc. cit.*, p. 286.

16. *a* ———— .. *Loc. cit.*, p. 286-87.

16. *b* ———— .. *Loc. cit.*, *p.* 287.

16. *c* ———— .. *Loc. cit.*, p. 287.

17. ———— .. *Loc. cit.*, 284.

18. William Ostwald .. " Iconoscopic Studies (Microscopic Identification of Homogeneous Binding Mediums)," translated, *Technical Studies*, 1935-36, **4**, 138-42.

19. Martin de Wild .. *The Scientific Examination of Pictures* (London : G. Bell & Sons, Ltd.), 1929.

Rutherford J. Gettens and G. L. Stout " The Stage Microscope in the Routine Examination of Paintings," *Technical Studies*, 1935-36, **4**, 224-28.

20. ———— .. " The Materials in the Wall Paintings of Bamiyan, Afghanistan," *Technical Studies*, 1938, p. 190.

21. Mary Hamilton Swindler *Ancient Painting* (New Haven : Yale University Press), 1929, p. 418.

22. A. P. Laurie .. *Greek and Roman Painting* (Cambridge : University Press), p. 83.

23. S. Paramasivan .. " The Mural Paintings in the Brihadisvara Temple at Tanjore—An Investigation into the Method," *Technical Studies*, 1936-37, **5**, p. 283.

CHEMICAL COMPOSITION OF INDIAN SENNA LEAVES (*CASSIA ANGUSTIFOLIA*)

By P. Bhaskara Rama Murti
and
T. R. Seshadri
(*From the Department of Chemical Technology, Andhra University, Waltair*)

Received August 8, 1939

The introduction of senna as an article of drug into the materia medica dates very far back. The Indian senna which is reputed for its high quality is extensively cultivated in the Southern districts of the Madras Presidency. Due to its commercial importance and the conflicting reports made by workers in the past regarding its composition it was considered desirable to re-examine the drug in detail.

The first systematic examination of the leaves was carried out by Tschirch and Hiepe.[1] From an aqueous percolate they claimed to have isolated an unstable yellowish crystalline compound of the composition, $C_{14}H_{10}O_5$, impure cathartic acid and senna-rhamnetin which was considered to be the same as iso-rhamnetin. From a dilute ammonia percolate they recorded that they obtained gluco-sennin, senna-emodin, senna chrysophanic acid and amorphous senna nigrin. Subsequently Tutin[2] made a more detailed analysis using an alcoholic extract. He divided it into two portions: (i) water-soluble portion, (ii) water insoluble resin. From the former he could isolate a glucoside of kæmpferol along with free kæmpferol, rhein, emodin and salicylic acid. From the resin he obtained fatty and waxy matter along with small quantities of kæmpferol, rhein and emodin. He was of opinion that cathartic acid and anthraglucosennin of Tschirch and Hiepe were impure mixtures. Further he could not detect the presence of any iso-rhamnetin or chrysophanic acid in the leaves. Though a number of papers have been published subsequently they are not of fundamental chemical importance and have not added to our knowledge of the chemical composition of the leaves.

There seems to exist considerable uncertainty regarding the nature of the inorganic salts present in senna. It is known that extractable inorganic salts can exert purgative action. During some of our experiments with water extracts, it was noticed that the addition of sulphuric acid precipitated a considerable amount of salts the main component of which was found to be calcium sulphate. Tutin was able to detect the presence of

magnesium salts. The ash of the entire leaves has therefore been analysed qualitatively and the important components estimated quantitatively. Most of the inorganic matter seems to be extractable with water. Calcium, magnesium and potassium exist as salts of organic acids and may account for a part of the purgative action of senna.

In our experiments on the isolation and characterisation of the organic compounds, it was found to be most convenient to remove the fatty and waxy matter at the beginning by extraction with light petroleum. By this means a good amount of such matter which would interfere with the isolation of other compounds at a later stage could be eliminated. From this extract was obtained after repeated purification using benzene, a colourless wax (senna wax) to the extent of more than 1 per cent. on the weight of the leaves. It could be divided into two fractions : (i) more sparingly soluble in benzene melting at 80–83° and found to be a wax-yielding myricyl alcohol as the main product of saponification ; (ii) more easily soluble in benzene melting at 87–88° consisting entirely of myricyl alcohol. Therefore it is clear that myricyl alcohol exists to a large extent in senna.

With a view to make a detailed examination of the flavonols, large quantities of the leaves extracted with light petroleum were employed. The alcoholic extracts of these leaves were divided into two fractions : (i) water-insoluble resin ; (ii) water-soluble material. Our preliminary experiments indicated that almost all of the flavonol portions went into the aqueous extract. This was therefore studied in detail by precipitating the pigments as the lead salts using neutral and basic lead acetates successively. It was convenient to use the two reagents since neutral lead acetate removed most of the resinous matter and subsequently when the bulk of the pigments was precipitated with the basic salt there was very little resin. The substances obtained by the decomposition of these lead salts were fractionally crystallised from alcohol. From the less soluble fraction a good yield of iso-rhamnetin could be obtained. The more soluble fraction yielded kæmpferol as the main component. It is therefore clear that iso-rhamnetin is an important component of the senna leaves and it is difficult to explain how Tutin failed to detect its presence in this material especially when it is present to the extent of nearly 50 per cent. of the flavonol mixture.

In the detailed study made by Tutin kæmpferol, emodin and rhein were obtained as mixtures at various stages requiring elaborate separation at each stage. The above procedure adopted by us yielded practically all the flavonols at one stage.

For isolating and examining the anthraquinone derivatives we have employed a different method. The whole of the alcoholic extract was subsequently extracted with boiling benzene, and then purified from resinous matter by repeated shaking with alkali, acidifying subsequently the alkaline solution and extracting again with benzene. By repeating this process, the anthraquinone derivatives were obtained in a pure condition (0·03%) and the mixture was found to consist mostly of rhein along with small quantities of emodin. It should be noted at this stage that of the three closely related anthraquinone derivatives rhein, emodin and chrysophanic acid, all the three were found by Tschrich and Hiepe, whereas the experiments of Tutin and ours indicate the presence of the first two only. It is probable that the occurrence of one or the other of these related compounds is dependent upon the conditions of soil and climate.

If in the process of isolating rhein outlined above a slight modification were introduced and the alcoholic extract boiled with hydrochloric acid prior to extraction with benzene the yield of rhein was almost doubled (0·07%). This could be explained as due to the existence of this anthraquinone compound in the leaf to a large extent as a glucoside insoluble in benzene.

Experimental

The leaves used for the present investigation were obtained from (The Agricultural Research Station) Koilpatti in the Tinnevelly District. The air-dried material was powdered in a grinder and preserved in glass stoppered jars.

The Ash.—The percentage of the ash in the leaves was determined by igniting the leaves in a platinum basin at a dull red-heat until a uniformly grey ash was obtained. It formed 9·6% by weight of the leaves and gave tests for the following radicals when analysed qualitatively : Iron, manganese, calcium, magnesium, potassium, sodium and phosphate, sulphate, carbonate, chloride and silicate. It was then analysed quantitatively for the important components. The following figures represent the amounts in terms of the oxides of the elements :

		%
SiO_2	(insoluble)	2·7
MgO	,,	7·2
CaO	,,	31·6
P_2O_5	,,	3·6

Isolation of Senna Wax.—4 kilo-grams of the leaf powder were extracted repeatedly with petroleum ether in a large continuous extractor,

until further extraction gave nearly a colourless solution. More than three-fourths of the solvent was distilled off and the concentrate allowed to stand. Since no crystalline product separated out of it even after several days, the remaining solvent was also removed as far as possible by distilling on a water-bath. The viscous green coloured residue could be purified best by employing benzene, other solvents and simple melting not being successful. It was taken in a wide-mouthed flask of 500 c.c. capacity and heated on a water-bath with sufficient benzene (250 c.c.) to give a clear solution. It was then quickly cooled with running water and kept undisturbed for 4 hours. A dark coloured solid gradually separated at the bottom. It was filtered and repeatedly washed with small amounts of benzene, whereby it was obtained in the form of a grey and non-sticky wax. It was then further purified by dissolving in a small quantity of hot benzene and allowing to crystallise. By repeating this process a number of times, fraction (I) was obtained in a perfectly colourless and crystalline form melting at 80–83° C.

The benzene mother-liquor and the subsequent washings were mixed together and concentrated to a small bulk. The solid that separated out was repeatedly recrystallised from benzene and thereby fraction (II) melting at 87–88 °C. was obtained.

Fraction I.—It was quite colourless, melted at 80–83° C. and formed nearly 1% of the weight of the dry leaves taken. It exhibited the properties of a wax. It was sparingly soluble in acetone, ether, chloroform, carbon tetrachloride and cold alcohol. It however readily dissolved in hot alcohol and when cooled separated in the form of a jelly-like mass. It had the following properties :

Saponification value	..	40·2
The acid value	..	5·2
Iodine value	..	2·1
Unsaponifiable matter	..	80%

The unsaponifiable matter was found to be identical in composition and properties with fraction (II) obtained from the benzene mother-liquor.

Fraction II : *Myricyl Alcohol.*—A preliminary examination of fraction (II) by heating it with seminormal alcoholic potash for 12 hours showed it to be completely unsaponifiable. It appeared to be a homogeneous compound and the analysis for carbon and hydrogen showed that it had the formula $C_{30}H_{62}O$ (Found : C, 82·0 ; H, 14·6 ; $C_{30}H_{62}O$ requires C, 82·2 ; H, 14·5%). From the melting point, it could be identified as myricyl alcohol. This was confirmed by preparing the acetyl derivative by heating it with sodium acetate and acetic anhydride for 5 hours, pouring the product

in a large volume of water and recrystallising the precipitate from ether. The acetyl derivative was obtained in the form of colourless plates melting at 70–71° C.

Isolation of Flavonols (Kæmpferol and Isorhamnetin)

The leaf powder left after extraction with petroleum ether was completely freed from the last traces of the solvent by blowing air through it. It was then repeatedly extracted with 95% alcohol till the process was complete. The dark coloured extract was concentrated to about 800 c.c. and filtered with suction. The filtrate was kept in a flask for several days but no crystalline product separated.

It was then poured into a large volume of water and the resinous mass that separated out was removed by filtration. The resin was again dissolved in alcohol and diluted with water when some more of it was brought into solution. This process was repeated thrice till all the water-soluble portion was extracted and the dark residue was finally rejected. The collected aqueous extract was concentrated to a small bulk under reduced pressure and allowed to stand for several days. Since it did not deposit any crystalline compound, it was treated in the following manner.

Neutral Lead Salt.—When treated with an excess of hot neutral lead acetate solution a dark brown precipitate was obtained. It was filtered and decomposed in the same way as the basic lead precipitate as described below. Besides large quantities of amorphous resin, it yielded the same flavonols and anthraquinone derivatives as the basic lead salt though in small amounts. The aqueous solution after hydrolysis responded to the tests for glucose and hence seemed to contain glucosides. This treatment with neutral lead acetate was found to be advantageous since it removed almost all resinous matter and rendered the subsequent study of the basic lead precipitate easy.

Basic Lead Salt.—The clear, brown filtrate obtained after the removal of the neutral lead precipitate, was boiled and treated with an excess of hot basic lead acetate solution. Even after the addition of a large amount of this reagent, it was found that all the colouring matter was not completely precipitated. By the cautious addition of a few c.c. of dilute ammonia, the precipitation was rendered complete. The canary yellow solid thus obtained was kept in fine suspension in water and decomposed by passing H_2S. The precipitated lead sulphide was removed by filtration and the resulting solution was concentrated under reduced pressure and finally allowed to evaporate in a desiccator. As no crystalline compound could be isolated from this after repeated attempts the whole of it was dissolved in water and hydrolysed with 7% sulphuric acid by heating the contents on

a water-bath. On cooling the flask a brown insoluble resin (A) separated. The clear solution obtained after the removal of the resin, was repeatedly ether-extracted and the mixed ether solution evaporated when an orange-yellow residue (B) was left behind. The remaining aqueous solution was found to contain glucose and hence the lead salt precipitate should consist of some glucosides.

Residue A.—The dark brown resin was not easily soluble in ether but readily dissolved in alcohol. To the alcoholic solution an excess of ether was added when a coloured resin separated. Since it yielded no crystalline solid on further treatment it was rejected. When the clear ether-alcohol solution was slowly concentrated a good amount of a clear orange yellow solid was obtained. It was found to be identical with residue (B) and the details of the experimental study are given below.

Residue B.—The material which was orange yellow in colour was found by a few preliminary tests to consist mostly of flavonol pigments along with small quantities of anthraquinone compounds. It was therefore dissolved in excess of alcohol and the solution was slowly concentrated as long as a clear yellow crystalline solid continued to separate. The mother-liquor (C) was turning darker red owing to the accumulation of the anthraquinone compounds. The crystalline solid melted between 280°–95° C., dissolved in aqueous alkali with a bright yellow colour and in concentrated sulphuric acid producing a deep blue fluorescence. It proved to be a mixture of flavonols (yield 0·1% of the leaves) and the separation was effected as below.

Isolation of Iso-rhamnetin.—The above mixture was subjected to fractional crystallisation using alcohol as solvent. The more sparingly soluble fraction was obtained in the form of greenish yellow crystals melting at 305–06° C. (Tutin gave the melting point as 302° and Heap and Robinson[3] 305°). The substance imparted a deep yellow colour to dilute alkali and its solution in concentrated sulphuric acid exhibited a green fluorescence. (Found : CH_3O, 9·4% ; required for $C_{16}H_{12}O_7$, 9·8%). By boiling it with acetic anhydride and sodium acetate, the acetyl derivative was obtained melting at 204°–05° C. thus confirming the identity of the compound with iso-rhamnetin.

Kæmpferol.—After the separation of iso-rhamnetin as above the alcohol mother-liquor was diluted with a few c.c. of water when a bright yellow crystalline substance was obtained. A little more of it was produced by slow concentration of the aqueous alcoholic solution. After further recrystallisation from dilute alcohol it appeared as tiny needle-shaped crystals and melted at 275°. With dilute alkali it gave a yellow colour and when

dissolved in concentrated sulphuric acid it gave a blue fluorescence which increased on standing. On acetylation with sodium acetate and acetic anhydride it formed an acetyl derivative which when recrystallised from alcohol gave colourless needle-shaped crystals melting at 120° C. On further heating it solidified and melted again at 182° C. This is a characteristic of kæmpferol acetate and hence the original flavonol was identified as Kæmpferol.

Separation of Anthraquinone Derivatives.—The red coloured mother-liquor (C) was evaporated so as to remove all alcohol and the residue was dissolved in a small quantity of ether. To the ether solution a large excess of petroleum ether was added when an orange yellow solid precipitated down. This was collected and dissolved in pyridine from which a small quantity of an orange yellow needle-shaped crystalline compound melting at 318°–20° C. was obtained. It gave red solutions with dilute alkali as well as with concentrated sulphuric acid. This was identified as rhein by comparison with an authentic sample. A mixture of the two did not show any depression in the melting point.

By evaporating the ether-petrol mother-liquor a small residue was obtained which when recrystallised from ethyl acetate yielded a very small amount of orange brown crystalline solid melting at 218° C. It exhibited the properties of emodin forming pink coloured solutions with alkali and sulphuric acid.

Isolation of Rhein.—Starting with a separate batch of senna-leaves, it was first extracted with petroleum ether and subsequently with methylated spirit as already described. The alcoholic solution was distilled in order to remove the solvent as completely as possible. The residue was then extracted with hot benzene repeatedly till all benzene-soluble portions were removed. The collected benzene extract was filtered and shaken in the cold with 1% potassium hydroxide solution. The alakli solution was separated and the extraction repeated till no more colouring matter could be removed by the alkali. The potash solution was then acidified with hydrochloric acid and the precipitate extracted with benzene. By repeated transference of colouring matter alternately into potassium hydroxide and benzene, it was rendered pure. Finally the benzene solution was shaken with aqueous sodium bicarbonate solution repeatedly till all rhein was extracted. On acidifying the bicarbonate solution an orange yellow solid was obtained which on recrystallisation from pyridine appeared as orange yellow needles, melting at 318°–20° C. and exhibited all the properties of rhein. Its acetyl derivative was obtained as yellow needles melting at 247° C. with decomposition.

By the above method the yield of rhein amounted to about 0·03% on the weight of the dry leaves. By adopting the following modification however a much higher yield (0·07%) of rhein could be obtained. This definitely indicates that a good portion of the rhein exists in the leaves in the form of a glucoside.

The alcoholic extract of the leaves was concentrated to a small bulk and treated with sufficient amount of concentrated hydrochloric acid so as to bring the acid concentration of the solution to 7%. It was then boiled for 2 hours and then distilled *in vacuo* to dryness. The residue was then extracted with benzene and the purification of rhein effected as already described.

The benzene solution from which rhein had been removed yielded a very small quantity of reddish brown solid on evaporation. It could be recrystallised from ethyl acetate when a pure substance melting at 218° C. and showing the properties of emodin was obtained. The quantity was however very small.

Summary

A detailed chemical examination of the Indian senna leaves has been made. The ash has been analysed. An aqueous extract of the leaves has been found to contain a good amount of calcium salts. A petroleum ether extract yields senna wax consisting of free myricyl alcohol admixed with regular wax. Methods have been worked out for obtaining the flavonol and anthraquinone group of compounds separately in the most convenient manner and in the best yield. The flavonol portion consists of iso-rhamnetin and kæmpferol in more or less equal quantities, whereas the anthraquinone portion contains mostly rhein along with small quantities of emodin.

REFERENCES

1. Tschirch and Hiepe .. *Arch. Pharm.*, 1900, **238**, 427.
2. Frank Tutin .. *J. Chem. Soc.*, 1913, 2006.
3. Tom Heap and Robert Robinson *Ibid.*, 1926, 2342.

1126-39—Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao Superintendent, and Published by The Indian Academy of Sciences, Bangalore